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# Lattice mechanical properties of noble metals

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**bstract** The application of a model pseudopotential due to Bretonnet and Silbert, which was shown to be extremely useful for liquid state roperties of transition metals and solid state properties of partly filled *d*-band metals Ni, Pd, and Pt [1], has been extended to calculate the lattice echanical properties of completely filled *d*-band metals, Cu, Ag and Au The calculation of phonon dispersion, Debye temperature, mean frequency, ean square frequency, maximum frequency, Debye-Waller factor, mean square displacement, elastic constants and mode Gruneisen parameters show at this model is better than previously reported models

**eywords** . Pseudopotential, lattice dynamics, noble metals

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## 1. Introduction

n a recent paper [1], we have shown that a model seudopotential due to Bretonnet and Silbert [2], which was ound to be highly successful in describing liquid state roperties of transition and non simple metals [3-6], can be used with equal degree of success to compute solid state properties of transition metals Ni, Pd and Pt. This potential, which contains the effects of *s*, *p* and *d* electrons was shown to reproduce satisfactorily, the phonon dispersion curves, Debye temperature, elastic constants, mode Gruneisen parameters of Ni, Pd and Pt. Encouraged by this fact we have, in the present work, undertaken the computation of lattice mechanical properties of completely filled *d*-band metals Cu, Ag and Au.

In this paper, we present the results of our calculations and compare them with the experimental data and results of other calculations [7-11]. It should be noted that the systematic calculations of both static and dynamic properties of these metals on the same footing are rare [7, 8].

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The bare ion model potential proposed by Bretonnet and Silbert [2], is given by

$$V_{ion}(r) = \sum_{n=1}^{2} B_n \, e^{-(r/na)}, \; r < R_c \qquad (1)$$

$$= -\frac{\sim_s}{r} \;, \quad r > R_c \;.$$

In $q$-space,

$$V_{ion}(q) = 4\pi a^3 \rho \Big| \frac{B_1 H_1}{(1+a^2q^2)^2} + \frac{8 B_2 H_2}{(1+4a^2q^2)^2}$$

$$\cdot \frac{4\pi Z s \rho}{\ldots^2} \cos q R_c \,, \qquad (2)$$

where $a$, $R_c$ and $\zeta$ stand for softness parameter, core radius and effective $s$-electron occupancy number, respectively. The term inside the core is obtained from $d$-band scattering phase shift by using an inverse scattering approach. This term takes care of the $d$-band effect. The coefficient $B_n$ depends on $a$, $R_c$ and $Z$. The expressions for $B'_n$s can be found in [2].

We have screened the above pseudopotential with the help of Lindhard dielectric function corrected for the local field

factor due to Taylor [12]. The parameter $R_c$ was calculated using relation [13]

$$R_c = 0.51 R_a Z_s^{-1/3} \quad (3)$$

The parameter $a$ and effective number of $s$-electron, $Z_s$ were adjusted to get an overall good fit to the experimental phonon dispersion curves at zero pressure. The parameters so evaluated were examined in their ability to satisfy the zero pressure condition at zero temperature. It was found that presently evaluated parameters do satisfy this condition. The values of the parameters for Cu, Ag and Au are given in Table 1. In the present calculations, we have followed Wallace [14] who has discussed in detail the methods of calculations of various static, dynamic and thermodynamic properties of crystal in harmonic approximation. In the present paper, we have also calculated the Debye-Waller factor and mean square displacement of Cu, Ag and Au. The relevant method of calculations may be found in Ref [15].

**Table 1.** Input parameters and pseudopotential parameters for noble metals

| Metal | Input-parameters | | Pseudopotential parameters (in a u) | |
|---|---|---|---|---|
| | Effective number of $s$-electron $Z_s$ | Atomic volume $\Omega$ (a u) | $R_c$ | $a$ |
| Cu | 1 40 | 79 68 | 1 341 | - 0 30 |
| Ag | 1 455 | 115 5 | 1 216 | - 0 42 |
| Au | 1 50 | 114 4 | 1.359 | - 0 60 |

## 2. Results and discussion

The phonon dispersion curves computed presently are shown in Figures [1-3] for Cu, Ag and Au respectively. The experimental points are due to Nilsson and Rolandsson [16] for Cu, Kamatikahara and Brockhouse [17] for Ag and Lynn *et al* [18] for Au. It can be seen that overall agreement between theory and experiment is fairly good. The maximum deviation, only at a few points, is about 10%. The temperature variation of Debye temperature for Cu, Ag, and Au is shown in Figure 4. The experimental points are due to Martin [19] for Cu, Meads *et al* [20] for Ag, and Martin [21] for Au. Again, the agreement between theory and experiment is fairly satisfactory.

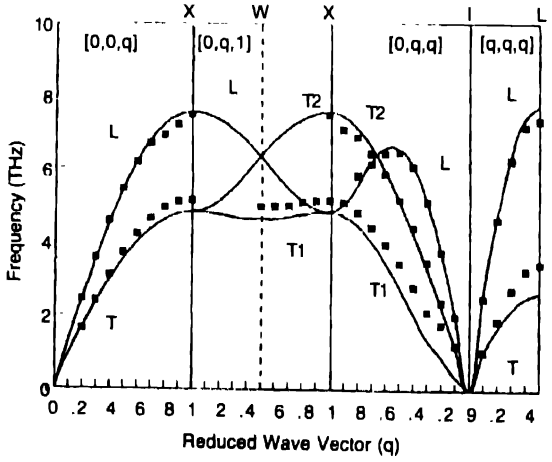



**Figure 1.** Phonon dispersion curves for Copper in symmetry directions

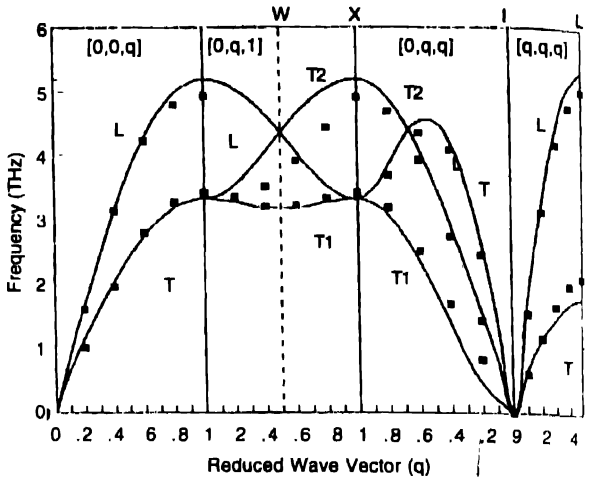



**Figure 2.** Phonon dispersion curves for Silver in symmetry directions. Experimental points are from Ref. [17]

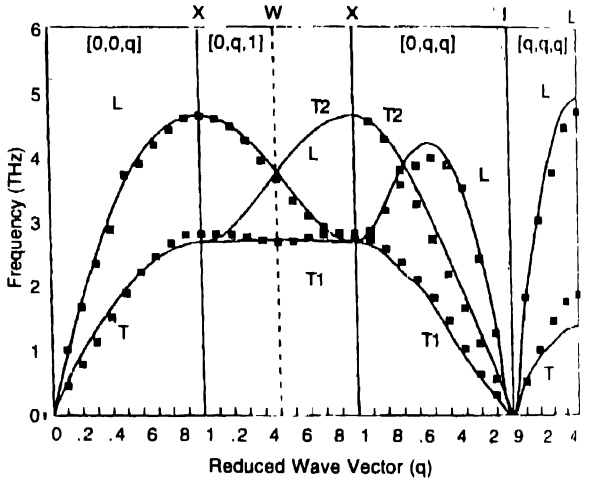



**Figure 3.** Phonon dispersion curves for Gold in symmetry direct Experiment points are from Ref [18]

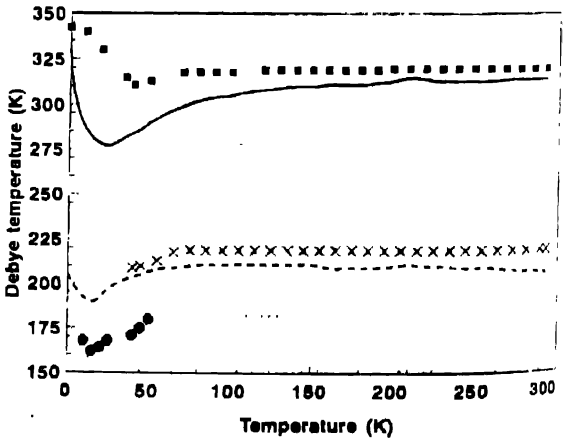



**Figure 4.** Debye temperature as a function of temperature for Cu (——), Silver (---) and Gold (. . .). The experimental points (■) are from Ref [19], experimental points for Silver (x) are from

Debye-Waller factor and mean square displacement of Cu, Ag and Au are presented in Figure [5-7]. Recently, Peng *et al* [22] have derived the Debye-Waller factor and mean square displacement for 44 elemental crystals from the experimentally determined phonon density of states. The experimental points in Figures [5-7] are those due to Peng *et al* [22]. In low temperature region, our results show fair agreement with the experimental results. However, particularly for Au, our results in the higher temperature region, differ appreciably from those of Peng *et al* [22].

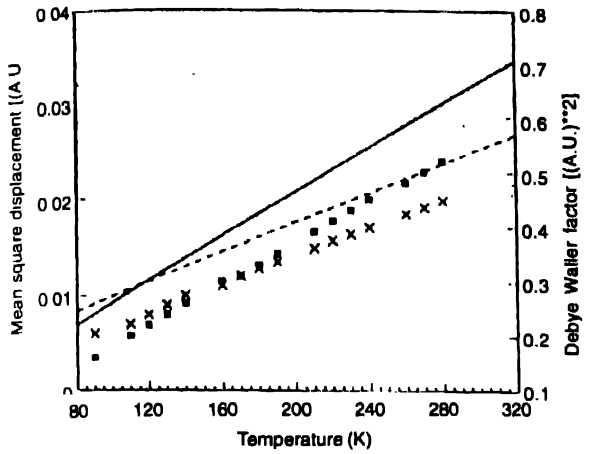
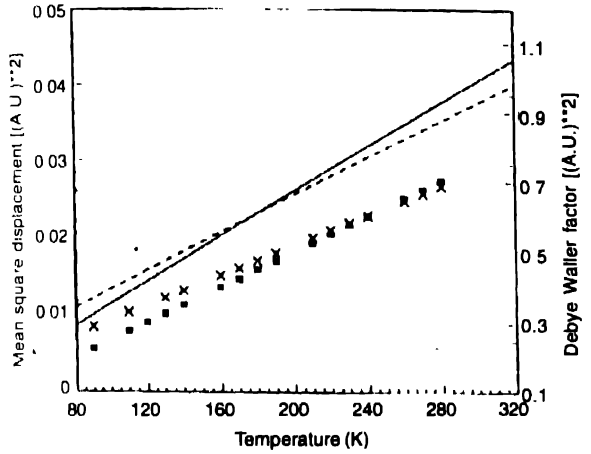
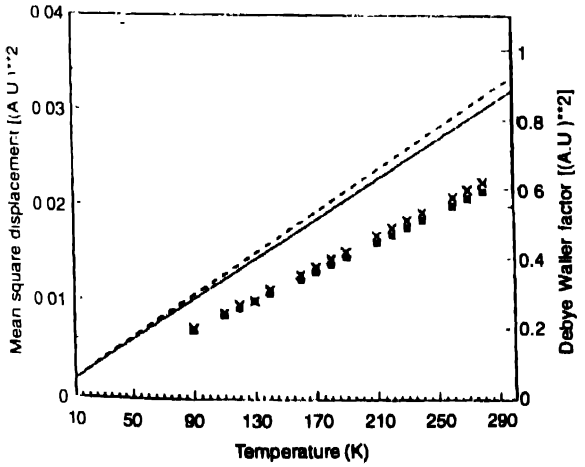



Figure 5. Debye-Waller factor (---) and mean square displacement ) for Copper The experimental points for Debye-Waller factor (■) and mean square displacement (x) are from Ref. [22].




igure 6. Debye-Waller factor (---) and mean square displacement ) for Silver The experimental points for Debye-Waller factor (■) nd mean square displacement (x) are from Ref. [22].




gure 7. Debye-Waller factor (---) and mean square displacement ) for Gold The experimental points for Debye-Waller factor (■) and an square displacement (x) are from Ref. [22].

There have been several model calculations on elastic constants of Noble metals. We compare our results in Table 2 with experiment [23] and other reported values [7-11]. It can be seen from the Table that most of the theoretical values computed presently compare well with experiment. In some cases, they are better than the other theoretical results. However, a comment regarding computed values of some elastic constants is in order. For Au, computed $C_{12}$ differs from its experimental value by about 40%. Also for Cu, the computed value of $C_{44}$ differs from the experimental value by about 33%. These differences may be due to the neglect of non-local effects and the higher order terms in the perturbation expansion in pseudopotential.

**Table 2.** Elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$) and bulk modulii (all in M bar) for noble metals

| | $C_{11}$ | $C_{12}$ | $C_{44}$ | $B$ |
|---|---|---|---|---|
| Cu | | | | |
| Present work | 1.828 | 0.951 | 1.09 | 1 244 |
| Exp. [23] | 1.762 | 1.249 | 0.817 | 1.420 |
| Antonov *et al* [7] | 0 909 | 0 499 | 0.817 | 0 635 |
| Khwaja and Razmi [9] | 1 610 | 1.182 | 0 770 | 1.324 |
| Kulshrestha *et al* [10] | 1.549 | 1 333 | 0.417 | 1 405 |
| Khanna [11] | 1.512 | 1.168 | 0.793 | 1 282 |
| Ag | | | | |
| Present work | 1.379 | 0.709 | 0 650 | 0 932 |
| Exp [23] | 1 315 | 0.573 | 0 511 | 1 087 |
| Antonov *et al* [7] | 1 076 | 0.528 | 0 475 | 0 710 |
| Khwaja and Razmi [9] | 1 182 | 1.021 | 0 498 | 1.074 |
| Kulshrestha *et al* [10] | 1.016 | 0.910 | 0.293 | 0.945 |
| Khanna [11] | 1 292 | 1 114 | 0 496 | 1 173 |
| Au | | | | |
| Present work | 2.040 | 1 019 | 0.510 | 1.360 |
| Exp. [23] | 2.016 | 1.697 | 0.454 | 1.080 |
| Antonov *et al* [7] | 1 804 | 1.272 | 0.400 | 1 449 |
| Khwaja and Razmi [9] | 1.887 | 1 634 | 0 484 | 1.718 |
| Kulshrestha *et al* [10] | 1.997 | 1.901 | 0 243 | 1.933 |
| Khanna [11] | | | | |

Looking to the fact that experimental values of elastic constants are uncertain by about 15%, the results presented in Table 2 are overall satisfactory.

In Table 3, we present the calculated values of mean frequency $<\omega>$, mean square frequency $<\omega^2>$ and maximum frequency $\omega_{max}$. These quantities represent the characteristic of density of phonon states. Except the values of $<\omega^2>$ for Cu and Ag, our results show reasonably good agreement with experiment and other reported values due to Antonov *et al* [7].

**Table 3.** Maximum phonon frequency $\omega_{max}$, mean frequency $<\omega>$ and $<\omega^2>$ for noble metals (all in THz)

| | | Cu | Ag | Au |
|---|---|---|---|---|
| | Present work | 50.24 | 32.76 | 29 01 |
| $\omega_{max}$ | Exp. | 46 78 | 31 56 | 29.51 |
| | | [16] | [17] | [18] |
| | Antonov *et al* [7] | 45.31 | 31 91 | 37 38 |
| | Present work | 28 26 | 19 50 | 16.69 |
| $<\omega>$ | Exp | 31 48 | 20 99 | 17 57 |
| | | [16] | [17] | [18] |
| | Antonov *et al* [7] | 30 60 | 22 25 | 20 31 |
| | Present work | 23 51 | 15 97 | 12 45 |
| $<\omega^2>$ | Exp | 32 03 | 19 55 | 15 84 |
| | | [16] | [17] | [18] |
| | Antonov *et al* [7] | 27 39 | 20 99 | 17 40 |

The mode Gruneisen parameters are presented in Figure [8-10] for Cu, Ag and Au respectively. Antonov *et al* [8] have calculated Gruneisen parameter for Cu [7]. Our values show a reasonable agreement with these results.

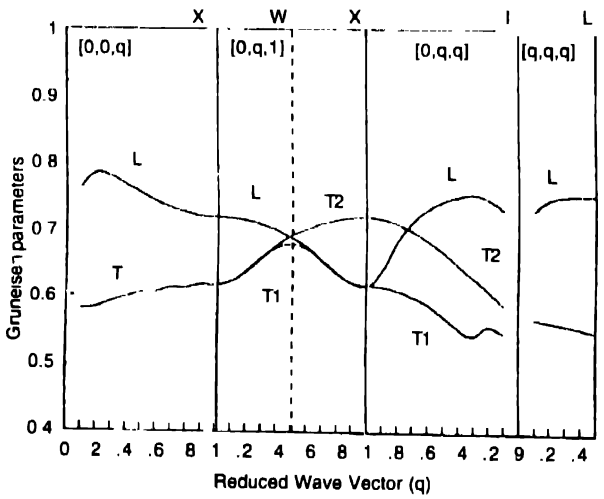



**Figure 8.** Mode Gruneisen parameter for Copper

## 3. Conclusion

We have successfully extended the [illegible] pseudopotential due to Bretonnet and Silbert [2] to solid noble metals. The calculations of several lattice mechanical properties

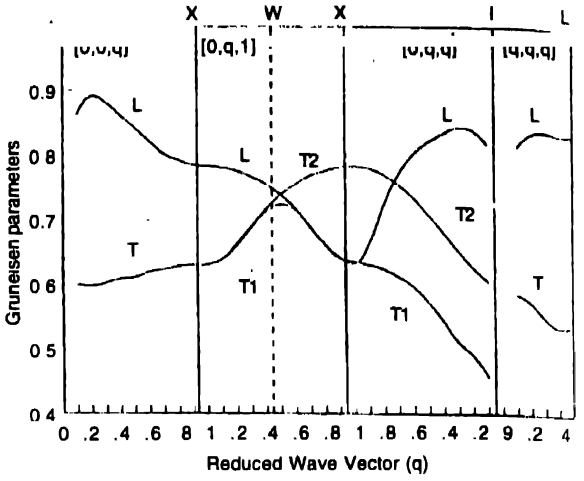



**Figure 9.** Mode Gruneisen parameter for Silver.

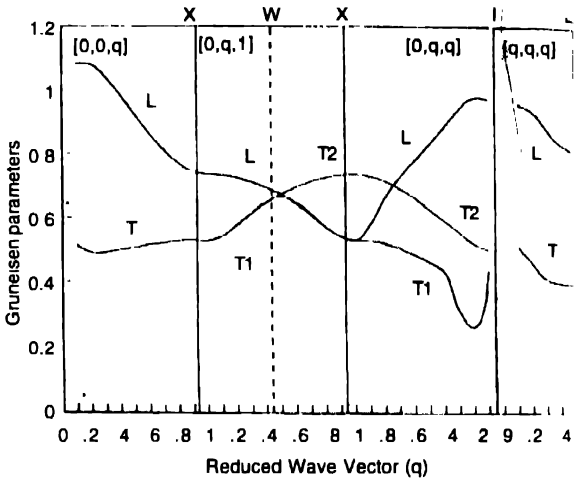



**Figure 10.** Mode Gruneisen parameter for Gold

(both static and dynamic) show that this model is in some respects better than the previously reported models (i) The model contains only two parameters. (ii) It is easy to use in numerical calculations. (iii) The model does not depend on any phenomenology. (iv) With this model, no other terms are required to simulate the *s–d* hybridization and overlap effects. Finally, we conclude that the present model is equally applicable to partly filled and completely filled *d*-band *fcc* transition metals

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